

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07B 63/04, C07C 7/20	A1	(11) International Publication Number: WO 98/02400 (43) International Publication Date: 22 January 1998 (22.01.98)
(21) International Application Number: PCT/GB97/01908 (22) International Filing Date: 15 July 1997 (15.07.97) (30) Priority Data: 9614854.9 15 July 1996 (15.07.96) GB (71) Applicant (for all designated States except US): A.H. MARKS AND COMPANY LIMITED [GB/GB]; Wyke, Bradford, West Yorkshire BD12 9EJ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): PRYCE, Anthony [GB/GB]; 14 Alexandra Road, Pudsey, Leeds, West Yorkshire LS28 8BY (GB). CALLIN, Robert, Charles [GB/GB]; 4 Margerison Road, Ben Rhydding, Ilkley LS29 8QU (GB). (74) Agent: BROWNE, Robin, Forsythe; Urquhart-Dykes & Lord, Tower House, Merrion Way, Leeds LS2 8PA (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: POLYMERISATION INHIBITOR (57) Abstract A monomer composition, stabilised against premature polymerisation, comprising: a) an ethylenically unsaturated monomer or mixture of monomers polymerisable by free radical initiation, and b) an effective amount, sufficient to inhibit premature polymerisation of component (a) of a mixture of: i) 1 to 99 % by weight, based on the total weight of components (i) and (ii) of a mixture of at least one aromatic amine and at least one organic acid in a molar ratio of 10:1 to 1:10, and ii) 99 to 1 % by weight based on the total weight of components (i) and (ii) of at least one stable radical compound.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

POLYMERISATION INHIBITOR

This invention relates to free radical scavengers for use as or in connection with inhibitors of olefinic polymerisation, particularly but not exclusively for inhibition of polymerisation of vinyl aromatic compounds.

Olefinic compounds such as butadiene, acrylic monomers, styrene and other vinyl aromatic compounds have a strong tendency to polymerise on storage or heating. High temperature techniques such as distillation are commonly used during separation and purification processes and the industrial production of these olefinic compounds.

Although free radical scavengers have been used to prevent olefinic polymerisation, there is a requirement for higher efficiency scavengers which may be used at lower concentrations or for scavengers which are more efficient at the same concentrations as are currently employed. Lower concentrations are economic, less toxic and are environmentally beneficial. More efficient compositions are economic, giving reduced wastage and/or prolongation of the active life of the olefin.

Various compounds and compositions have been used as free radical scavengers to prevent or reduce undesired polymerisation of olefinic compounds during high temperature processes. These inhibitors have given varying degrees of success. In a typical process an olefinic compound may be contacted with the inhibitor before distillation or other processing. However the amount of polymer formed during such processing may be substantially higher than desired, leading to economic loss. In other cases it may be possible to achieve economically desirable low levels of polymerisation but only by use of economically unacceptable quantities of the inhibitor. Sulphur has been widely employed as a polymerisation inhibitor but difficulties in handling and disposal have lead to replacement by non-sulphur inhibitors, referred to as NSIs. SU-A-819078 discloses use of 3,5-ditertiary butyl-4-oxy-N,N-

-2-

dimethylbenzylamine in combination with a C₁₀-C₂₀ aliphatic carboxylic acid. However the concentrations of this particular NSI are sufficiently large (500 to 2200 ppm) that much of the NSI is not consumed in a typical process. This results in uneconomic quantities of residual NSI being present in the effluent or waste from the process. EP-A-550754 discloses a polymerisation inhibitor for vinyl compounds combining a reaction product of 4-(dimethylamino)methyl-2,6-bis(tert butyl)phenol with an inorganic or carboxylic acid in the weight ratio 1 to 15:3. WO95/03263 discloses reduction in the quantity of this NSI by use in combination with air. However it is undesirable to introduce air into many high temperature processes involving olefinic compounds. Firstly there is an economic cost associated with ensuring a supply of the required quantity of air. Secondly it is often a safety hazard to introduce air into the stream of a hot olefinic compound due to the risk of oxidation, fire or an explosion.

Use of stable free radicals for inhibiting polymerisation by scavenging other free radicals has been disclosed. G M Burnett, Mechanism of Polymer Reactions, Interscience, New York 1954, 76, stated that a sterically hindered nitroxyl radical, 2,2,6,6-tetramethyl piperidiny1-1-oxyl (referred to as TEMPO) is effective against carbon centred radicals. Use of stable free radicals as scavengers was reviewed by E G Rozantsev, Free Nitroxyl Radicals, Plenar Press, 1970, 105. The practical utility of nitroxyl radicals as scavengers to prevent polymerisation was disclosed in GB 1127127 and GB 1218456. The high cost of stable free radicals has restricted their commercial use and there remains a requirement for an economic means of preventing or controlling polymerisation. US 4670131 disclosed that certain stable free radicals may be used as polymerisation inhibitors under certain conditions at levels less than 700 parts per billion. However such low usage rates are not of general applicability.

We have now found that a free radical scavenger composition including an aromatic amine in combination with an organic acid and a stable free radical compound is effective

without the economic disadvantages of the previously disclosed compositions.

According to a first aspect of the present invention a monomer composition, stabilised against premature polymerisation, comprises:

a) an ethylenically unsaturated monomer or mixture of monomers polymerisable by free radical initiation, and

b) an effective amount, sufficient to inhibit premature polymerisation of component (a) of a mixture of:

i) 1 to 99% by weight, based on the total weight of components (i) and (ii) of a mixture of at least one aromatic amine and at least one organic acid in a molar ratio of 10:1 to 1:10, and

ii) 99 to 1% by weight based on the total weight of components (i) and (ii) of at least one stable radical compound.

Compositions in accordance with this invention exhibit a synergistic effect in that the inhibition efficiency is greater than that of the two components. Preferred monomers are vinyl aromatic compounds for example styrene, methyl styrene, vinyl toluene or divinyl benzene or vinyl aliphatic compounds including acrylonitrile, acrylic acid, methacrylic acid, acrylate esters, methacrylate esters, butadiene and butenes. The invention is particularly applicable in inhibition of polymerisation of styrene during distillation, purification or storage.

In preferred compositions the weight of component i) is 50 to 99% and the weight of component ii) is 50 to 1%. In particularly preferred embodiments of the invention the weight of component i) is 67 to 99% and the weight of component ii) is 33 to 1%.

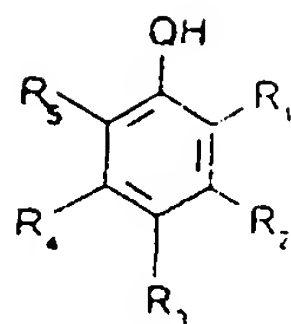
Percentages and other amounts in this specification are by weight unless indicated otherwise. Percentages and other proportions are selected to total 100%.

The molar ratio of said at least one aromatic amine to said at least one organic acid is 3:1 to 1:3.

In preferred embodiments of the invention the aromatic

-4-

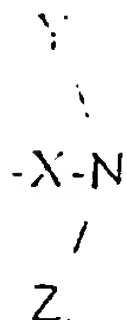
amine has the formula (1)



(1)

wherein Q is O or S or N-Z

and wherein at least one R is an alkyl amine of the structure (2)



(2)

in which Y, Z are the same or different and comprise C₁ to C₃ branched or straight chain alkyl or hydrogen and in which X is either a covalent bond or C₁ to C₄ alkylene, and wherein each remaining R is independently benzyl, C₁ to C₄ branched or straight chain alkyl or hydrogen with the provision that two or more R may be connected to form one or more rings.

Q is preferably oxygen.

X is preferably methylene.

Y and Z are preferably methyl.

R¹ and R⁵ are preferably tertiary butyl.

A preferred amine has Y and Z as methyl and R³ and R⁴ as hydrogen.

Preferred amines include benzylamine and benzylamine derivatives, for example 3,5-tertiarybutyl-4-hydroxybenzylamine, anilines and phenylene diamines, for example

N,N-dimethyl-1,4-phenylenediamine

3,5-ditertiarybutyl-4-oxy, N,N-dimethylbenzylamine

3,5-ditertiarybutyl-4-oxy-N,N-diethylbenzylamine

-5-

N,N-dimethyl-2,6-ditertiarybutyl-4-amino phenol

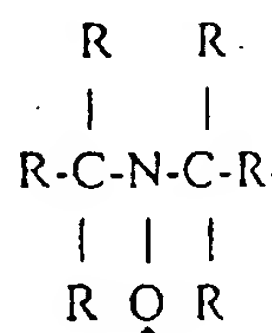
1,4-phenylenediamine

N,N-dimethyl-4-aminothiophenol

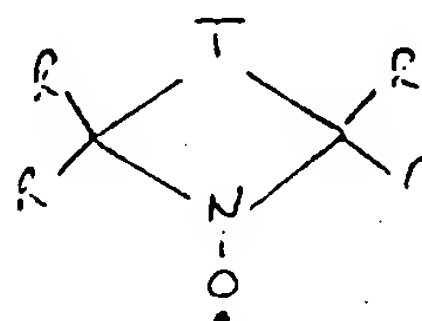
N,N'-bis-(1,4 dimethylpentyl)-1,4-phenylenediamine

In preferred embodiments of the invention the organic acid is a carboxylic acid. C_6 to C_{22} , preferably C_6 to C_{18} saturated or unsaturated carboxylic acids are particularly efficacious. These may be substituted with groups inert to attack by the nitroxyl radical. Linear or branched chain acids may be employed. Branch chain acids which are liquid at ambient temperatures are convenient to manipulate. Unsubstituted saturated acids are especially preferred.

The stable radical compound is preferably a sterically hindered nitroxyl of the formulae (3)

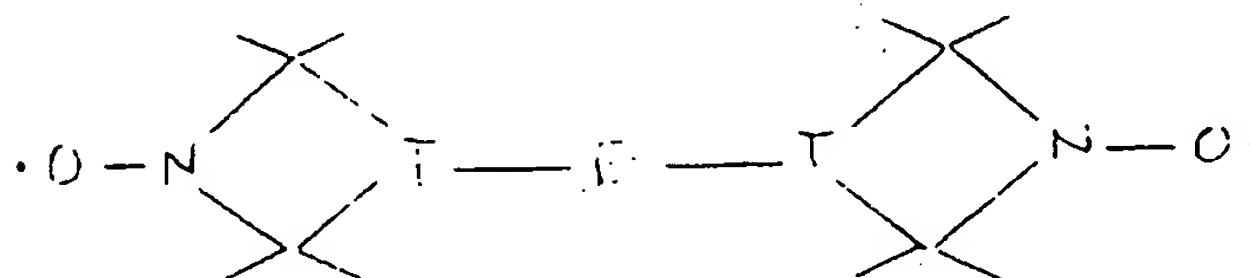


or



(3)

or



wherein R is hydrogen, alkyl or aryl and T is a group required to form a ring and wherein two or more T groups may be linked by a linking group E.

Preferred nitroxyl compounds may be selected from:

1-oxyl-2,2,6,6-tetramethylpiperidin,

1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol,

1-oxyl-2,2,6,6-tetramethylpiperidin-4-one,

1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetate,

1,oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-

-6-

ethylhexanoate,

1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl stearate,

1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl benzoate,

1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 4-tert-butylbenzoate,

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) succinate,

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) adipate,

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) n-butylmalonate,

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) phthalate,

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) isophthalate,

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) terephthalate,

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) hexahydroterephthalate,

N,N'-bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) adipamine,

N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) caprolactam,

N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) dodecylsuccinimide

2,4,6-tris-[N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)]-s-triazine, and

4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperidin-3-one)

4-acetylamino 2,2,6,6-tetramethylpiperidin-N-oxyl

Most preferably, the compound of component b) is

1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol, or

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate

Preferred nitroxyl compounds are piperidinoxyl compounds.

According to a second aspect of the present invention a process for inhibiting premature polymerisation of a vinyl aromatic or aliphatic compound during distillation, purification or storage, comprises the step of incorporating therein an effective inhibiting amount, sufficient to prevent

premature polymerisation during distillation, purification or storage of a mixture of

i) 1 to 99% by weight, based on the total weight of components (i) and (ii), of an admixture of at least one aromatic amine and at least one organic acid in a molar ratio of from 10:1 to 1:10 and

ii) 99 to 1% by weight, based on the total weight of components (i) and (ii), of at least one stable radical compound.

Preferred processes of this invention use a stabilising composition which is synergistic in nature, that is using half the concentration of component a) together with half the concentration of component b) to afford a greater stabilisation efficacy than may be achieved using either component a) or b) alone.

Preferred processes in accordance with this invention employ stabilising compositions as described above with reference to the first aspect of this invention.

The effective amount of polymerisation inhibitors employed may vary over a wide range depending upon the particular olefinic compound and the distillation or other purification conditions employed. Preferably the total amount of an aromatic amine and an aliphatic carboxylic acid and a stable free radical is from 1 ppm to 2000 ppm based upon the weight of the olefinic compound. For most olefinic compounds the mixture of components a) and b) is 5 to 1000 ppm. Greater amounts of inhibitor are required at higher temperatures. During distillation of olefinic mixtures the temperature of the reboiler may be up to about 150°C. Since the boiling points of the various aromatic amines of component a) and of the various stable free radicals b) are different, compounds which have the desired boiling points can be easily selected. The compositions of this invention which inhibit the polymerisation of the olefinic compound are also well suited for protecting the re-boiler sections of a distillation column or the compressor sections before entering a distillation column.

The polymerisation inhibitor can be introduced into the olefinic compound to be protected by any conventional method. It may be added as a concentrated solution in a suitable solvent. Since the solubilities of the various aromatic amines of component a) of the various organic acids of component a) and of the various stable free radicals of component b) are different, compounds which have the desired solubilities can be easily selected. The components a) and b) may be injected separately into the distillation train along with the incoming feed, or through separate entry points providing there is an efficient distribution of the inhibitors.

The inhibitors are gradually depleted during the distillation operation. Consequently it is generally necessary to maintain the appropriate amount of inhibitor mixture in the distillation apparatus by adding inhibitors during the course of the distillation process. Such addition may be carried out either on a generally continuous basis or it may consist of intermittently charging inhibitor into the distillation system in order to maintain the concentration of the inhibitor in excess of the minimum required level. The amine and carboxylic acid may be added separately at different entry points into the process stream.

The present invention enables the distillation and purification of olefinic compounds in manufacturing plants to operate more economically compared to prior art processes because of the greater effectiveness with or without the presence of oxygen. This permits lower inhibitor usages with minimal polymer formation.

The present invention also enables the storage of olefinic compounds for prolonged periods of time at ambient or elevated temperatures with or without the presence of oxygen by utilising economically beneficial amounts of the scavenger composition to minimise polymer formation.

The present invention is further described by means of example but not in any limitative sense.

Examples 1 to 3

Commercial quality styrene was washed with dilute caustic soda solution to remove the storage stabiliser, tert-butylcatechol. The styrene was then washed with water to remove excess alkali, following which it was dried over anhydrous sodium sulphate prior to use as follows;

Inhibitor and styrene (enough to make total weight of mixture of 200 g) were charged to a 250 ml round-bottomed flask fitted with an overhead stirrer, thermometer, sparge tube and water cooled condenser (see diagram below). The stirrer was started. Nitrogen (200 ml min^{-1}) sparging through the reaction mixture was then applied. The reaction mixture was then heated to 100°C using an oil bath, and stirred at this temperature for two hours. Samples were removed and analysed for polystyrene content using a spectrophotometric method at 420 nm. The analysis method was based on American Standard Test Method D2121 and a calibration was made using authentic polystyrene in styrene solutions of known concentrations by weight. In a controlled experiment, without any inhibitor present much greater than 30000 ppm (limit of quantification) of polystyrene was formed. Polymer levels obtained with various inhibitors present are shown in the table below. The blends of inhibitors were considerably more effective at reducing the amount of polymer formed than were either of the components when used individually at the full rate of inhibitor concentration. This clearly demonstrates that an unexpected synergistic effect occurs in the polymerisation inhibition of styrene in the absence of air by using both an aromatic amine-aliphatic carboxylic acid inhibitor and a stable free radical inhibitor together as compared to using either inhibitor alone at twice its concentration found in the combination.

Example No	Inhibitors	ppm	Polymer (ppm)
Control	None	---	>30,000
1	A	33	23 448
2	B	517	754
3	A plus B	17 plus 258	50

A is 4-hydroxy-2,2,6,6-tetramethyl-piperidinyl-1-oxyl radical.
 B is 3,5-ditertiarybutyl-4-oxy, N,N-dimethylbenzylamine in combination with stearic acid (molar ratio 1:1.5).

Examples 4 to 6

The procedure of Examples 1 to 3 was repeated with a higher test temperature of 115°C and instead of a nitrogen sparge there was applied an air sparge (4 ml min⁻¹). The results of these tests are shown below;

Example No	Inhibitors	ppm	Polymer (ppm)
4	A	33	28 000
5	B	517	3 000
6	A plus B	17 plus 258	1 684

A is 4-hydroxy-2,2,6,6-tetramethyl-piperidinyl-1-oxyl radical
 B is 3,5-ditertiary butyl-4-oxy-N,N-dimethylbenzylamine in combination with stearic acid (molar ratio 1:1.5).

There is a clear synergistic inhibiting effect on the polymerisation of styrene in the presence of air. When a mixture of the two inhibitor compounds are used together as compared to using either inhibitor alone at twice its concentration used in the combination.

Examples 7 to 9

The procedure of Examples 1 to 3 was repeated and instead of nitrogen sparge there was applied an air sparge (4 ml min^{-1}).

Example No	Inhibitors	ppm	Polymer (ppm)
7	A	10	14
8	C	150	18,230
9	A plus C	5 plus 75	0

A is 4-hydroxy-2,2,6,6-tetramethyl-piperidiny1-1-oxy radical
C is 3,5-ditertiary butyl-4-oxy N,N-dimethylbenzylamine in combination with stearic acid (molar ratio 1:3)

Examples 10 to 12

The procedure of Examples 7 to 9 was repeated but the time at 100°C was 1 hour instead of 2 hours.

Example No	Inhibitors	ppm	Polymer (ppm)
10	A	2	1,562
11	D	30	1,684
12	A plus D	1 plus 15	49

A is 4-hydroxy-2,2,6,6-tetramethyl-piperidiny1-1-oxy radical
D is 1,4-phenylenediamine in combination with stearic acid (molar ratio 1:1.5)

Examples 13 to 15

The procedure of Examples 4 to 6 was repeated but the time at 115°C was 1 hour instead of 2 hours.

-12-

Example No	Inhibitors	ppm	Polymer (ppm)
13	A	10	23,274
14	E	150	101
15	A plus E	5 plus 75	0

A is 4-hydroxy-2,2,6,6-tetramethyl-piperidiny1-1-oxy radical
E is N,N-bis-(1,4-dimethylpentyl)-1,4-phenylenediamine in combination with stearic acid (Molar Ratio 1:1.5)

Examples 16 to 21

The procedure of Examples 1 to 3 were repeated but a molar equivalent quantity of capric/caprylic acid was used in place of the stearic acid without any significant difference in the results.

Examples 22 to 24

The procedures of Examples 4 to 6 were repeated but a molar equivalent quantity of capric/caprylic acid was used in place of the stearic acid without any significant difference in the results.

Examples 25 to 27

The procedures of Examples 7 to 9 were repeated.

Example No	Inhibitors	ppm	Polymer (ppm)
25	F	10	414
26	B	150	19,970
27	F plus B	5 plus 75	397

B is 3,5-ditertiarybutyl-4-oxy-N,N-dimethylbenzylamine in

-13-

combination with stearic acid (Molar Ratio 1:1.5)
F is ditertiary butyl nitroxide.

CLAIMS.

1. A monomer composition, stabilised against premature polymerisation, comprising:

a) an ethylenically unsaturated monomer or mixture of monomers polymerisable by free radical initiation, and

b) an effective amount, sufficient to inhibit premature polymerisation of component (a) of a mixture of:

i) 1 to 99% by weight, based on the total weight of components (i) and (ii) of a mixture of at least one aromatic amine and at least one organic acid in a molar ratio of 10:1 to 1:10, and

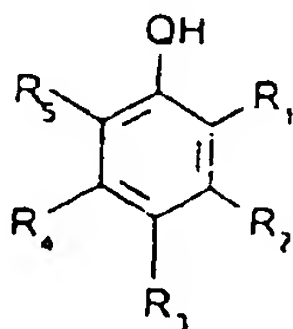
ii) 99 to 1% by weight based on the total weight of components (i) and (ii) of at least one stable radical compound.

2. A composition as claimed in claim 1, wherein the weight of component (i) is 50 to 99% and the weight of component (ii) is 50 to 1%.

3. A composition as claimed in claim 2, wherein the weight of component (i) is 67 to 99% and the weight of component (ii) is 33 to 1%.

4. A composition as claimed in any preceding claim, wherein the molar ratio of the aromatic amine to organic acid is 3:1 to 1:3.

5. A composition as claimed in any preceding claim, wherein the aromatic amine has the formula (1)



(1)

-15-

wherein Q is O or S or N-Z

and wherein at least one R is an alkyl amine of the structure
(2)



in which Y, Z are the same or different and comprise C₁ to C₈ branched or straight chain alkyl or hydrogen and in which X is either a covalent bond or C₁ to C₄ alkylene, and wherein each remaining R is independently benzyl, C₁ to C₄ branched or straight chain alkyl or hydrogen with the provision that two or more R may be connected to form one or more rings.

6. A composition as claimed in claim 5, wherein Q is oxygen.

7. A composition as claimed in claim 5 or 6 wherein in X is methylene.

8. A composition as claimed in any of claims 5 to 7, wherein Y and Z are methyl.

9. A composition as claimed in any preceding claim, wherein the amine is selected from

N,N-dimethyl-1,4-phenylenediamine

3,5-ditertiarybutyl-4-oxy, N,N-dimethylbenzylamine

3,5-ditertiarybutyl-4-oxy-N,N-diethylbenzylamine

N,N-dimethyl-2,6-ditertiarybutyl-4-amino phenol

1,4-phenylenediamine

N,N-dimethyl-4-aminothiophenol

N,N'-bis-(1,4 dimethylpentyl)-1,4-phenylenediamine.

10. A composition as claimed in any preceding claim,

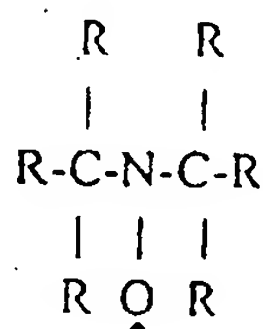
-16-

wherein the organic acid is a carboxylic acid.

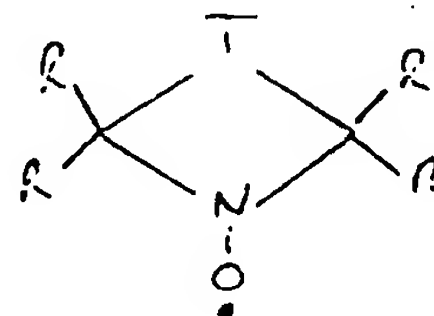
11. A composition as claimed in claim 10, wherein the organic acid is a C₆ to C₂₂ carboxylic acid.

12. A composition as claimed in claim 11, wherein the organic acid is a C₆ to C₁₈ carboxylic acid.

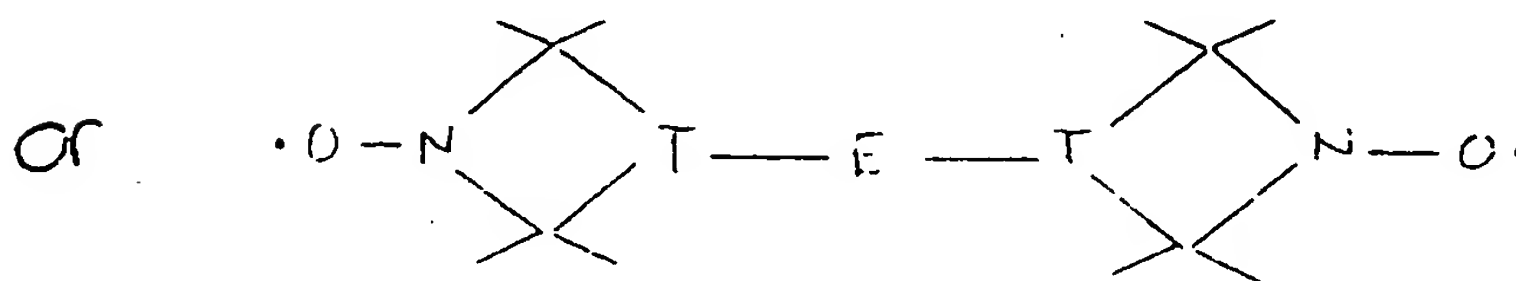
13. A composition as claimed in any preceding claim, wherein the stable radical compound is a sterically hindered nitroxyl of formulae 3



OR



(3)



wherein R is hydrogen, alkyl or aryl and T is a group required to form a ring and wherein two or more T groups may be linked by a linking group E.

14. A composition as claimed in claim 13, wherein the nitroxyl compound is selected from:

- 1-oxyl-2,2,6,6-tetramethylpiperidine,
- 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol,
- 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one,
- 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetate,
- 1,oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-ethylhexanoate,

-17-

1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl stearate,
1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl benzoate,
1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 4-tert-
butylbenzoate,
bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) succinate,
bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) adipate,
bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) n-
butylmalonate,
bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) phthalate,
bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)
isophthalate,
bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)
terephthalate,
bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)
hexahydrotetraphthalate,
N,N'-bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)
adipamine,
N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) caprolactam,
N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-
dodecylsuccinimide
2,4,6-tris-[N-butyl-N-(1-oxyl-2,2,6,6-
tetramethylpiperidin-4-yl)]-s-triazine, and
4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperidin-3-
one)
4-acetylamino 2,2,6,6-tetramethylpiperidin-N-oxyl.

15. A composition as claimed in claim 14, wherein the nitroxyl is 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol, or bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

16. A process for inhibiting premature polymerisation of a vinyl aromatic or aliphatic compound during distillation, purification or storage, comprising the step of incorporating therein an effective inhibiting amount, sufficient to prevent premature polymerisation during distillation, purification or

-18-

storage of a mixture of

i) 1 to 99% by weight, based on the total weight of components (i) and (ii), of an admixture of at least one aromatic amine and at least one organic acid in a molar ratio of from 10:1 to 1:10 and

ii) 99 to 1% by weight, based on the total weight of components (i) and (ii), of at least one stable radical compound.

17. A process as claimed in claim 16, wherein said mixture is selected to provide a composition in accordance with any of claims 1 to 15.

18. A process as claimed in claim 16 or 17.

INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No

PCT/GB 97/01908

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07B63/04 C07C7/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 03263 A (UNIROYAL) 2 February 1995 cited in the application see claims; examples ---	1-18
A	EP 0 550 754 A (NIZH. PROIZVOD. OBIED. "NIZHNEKAMSKNEFTEKHIM") 14 July 1993 cited in the application see the whole document ---	1-18
A	EP 0 697 386 A (HÜLS) 21 February 1996 see the whole document ---	1-18
A	US 5 254 760 A (R. A. E. WINTER) 19 October 1993 see the whole document -----	1-18

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

6 October 1997

Date of mailing of the international search report

1 3. 10. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl
Fax: (+31-70) 340-3016

Authorized officer

Wright, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Appl. No.
PCT/GB 97/01908

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9503263 A	02-02-95	RU 2075468 C US 5488192 A AU 7237094 A BR 9407148 A EP 0710222 A JP 9504509 T	20-03-97 30-01-96 20-02-95 17-09-96 08-05-96 06-05-97
EP 550754 A	14-07-93	WO 9302028 A KR 9604882 B	04-02-93 16-04-96
EP 697386 A	21-02-96	DE 19515450 A CN 1119636 A CZ 9502114 A JP 8059524 A PL 310071 A	22-02-96 03-04-96 15-05-96 05-03-96 04-03-96
US 5254760 A	19-10-93	AU 4425093 A BR 9303023 A CA 2101359 A CN 1084155 A DE 69310044 D EP 0581737 A ES 2101995 T JP 6166636 A MX 9304506 A	03-02-94 15-03-94 30-01-94 23-03-94 28-05-97 02-02-94 16-07-97 14-06-94 31-01-94